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SEMINAR SUMMARY: SAMPLING AND ANALYSIS OF THE VARIOUS FORMS OF ATMOSPHERIC LEAD

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The sampling and analysis of hazardous substances in the atmosphere are topics that currently generate substantial interest. One such hazardous substance, lead, was the subject of a day-long seminar wherein 10 prominent scientists knowledgeable in the areas of sampling and analysis of the various forms of atmospheric lead gave oral presentations. The seminar provided an opportunity to review the current methods for sampling and analyzing atmospheric lead and to consider recent research data by two seminar participants which suggest that certain forms of atmospheric lead pass through filters presently being used for measurement. The importance of this observation stems from the belief that if such lead exists it is likely to be much more physiologically active than particulate lead. This report summarizes those various presentations.

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SEMINAR SUMMARY:

SAMPLING AND ANALYSIS OF THE VARIOUS FORMS OF ATMOSPHERIC LEAD

INTRODUCTION

Scientists at the Environmental Protection Agency's National Environmental Research Center, located in the Research Triangle Park, N.C., have long been interested in the analysis of atmospheric pollutants. Of special interest are those hazardous substances found in fairly high concentrations in blood samples obtained from high-risk groups in various parts of the country. One such pollutant--well known for its toxicity--is lead, which was the subject of an informal, day-long seminar at the EPA facility on September 16, 1974.

The objectives of this seminar were twofold: (1) to provide a useful and timely review of current methods for sampling and analyzing atmospheric lead; and (2) to consider the latest research data by Drs. Robinson and Skogerboe which suggest that large quantities of lead pass through the filters presently being used to measure lead in the air.

The seminar, entitled Sampling and Analysis of the Various Forms of Atmospheric Lead, included oral presentations by ten prominent scientists knowledgeable in the problem area. A question-and-answer session was held after each presentation. This report is a summary of those informal presentations. The names of the participants and their affiliations are listed below.

1. James W. Robinson, Professor of Chemistry, Louisiana State University, Baton Rouge, Louisiana.

2. R.K. Skogerboe, Professor of Chemistry and Atmospheric Science, Colorado State University, Fort Collins, Colorado.

3. Reed Robertson, Senior Group Leader of the Environmental Services Laboratory, Nalco Chemical Co., Chicago, Illinois.

4. James Hickey, Director of Analytical Services Dept., Nalco Chemical Co., Chicago, Illinois.

5. Gary Ter Haar, Senior Research Associate, Petroleum Chemicals Research, Ethyl Corp., Detroit, Michigan.

6. Manuel Brandt, Superintendent of Chemical Analysis, Petroleum Chemicals Research, Ethyl Corp., Detroit, Michigan.

7. Ralph Parod, Ph.D. candidate in Physiology at Wayne State University. (Represented Environmental Health Laboratories, Inc., Farmington, Michigan.)

8. E.S. Jacobs, Superintendent of Automotive Emissions Division, DuPont Petroleum Laboratory, Deepwater, New Jersey.

9. Clair C. Patterson, Senior Research Associate, Geochemistry Division of Geological and Planetary Sciencies, California Institute of Technology, Pasadena, California.

10. Benjamin Y.H. Liu, Professor and Director, Particle Technology Laboratory, Mechanical Engineering Dept., University of Minnesota, Minneapolis, Minnesota.

PRESENTATIONS

James W. Robinson -- Louisiana State University

The instrument used for the determination of particulate and molecular atmospheric lead was described by Dr. Robinson as being a flameless atomic absorption device equipped with a 10-mm Micropore carbon disc (0.01-μm pore size) on the inlet port to filter the particulates, followed by an atomizer carbon bed to adsorb the molecular species. Dr. Robinson discussed data on particulate and molecular lead collected on 5 separate days with this instrument. Feasibility studies were carried out on 2 days to see if there was a detectable correlation between atmospheric molecular lead concentration and automobile traffic density. The next 3 days were "all-day" runs to ascertain any diurnal pattern of lead concentration fluctuation.

The results of the experiments described above showed that near a parking lot a large proportion of the lead was molecular (in the vapor phase, as opposed to extremely small particles). In addition, Dr. Robinson presented slides which showed that the diurnal maxima for molecular lead corresponded to peak traffic periods, and that during windless, high-humidity conditions, the molecular lead built up to very high concentrations (>50 $\mu g/m^3$). Dr. Robinson's explanation for this phenomenon was that lead from the exhaust deposits on the road and is then volatized under appropriate conditions of sunlight and humidity.

The speaker indicated that the data obtained on lead by the collection of particulates from the air with the use of high-volume samplers present only a partial atmospheric profile because the concentration of the molecular species of the metal is ignored. Further, the speaker pointed out that he has also found "molecular" compounds of cadmium, arsenic, zinc, and selenium using the collection system described, and that these molecular pollutants might also exist in concentrations significantly higher than are currently known. Dr. Robinson concluded that much more work needs to be done before recommendations are made.

R.K. Skogerboe -- Colorado State University

Dr. Skogerboe described a number of experiments to determine filter collection efficiencies for several elements, including lead. Initial field experiments set up at various distances from a busy street in Fort Collins, Colorado, used sampling trains consisting of a millipore filter (0.45-μm pore size) and two nitric acid scrubbers connected in series. The sampling trains were operated simultaneously and continuously for an average of 8 hours/day at a constant flow rate of 1 liter/minute, which corresponds to a total air volume of 0.48 m^3. Atomic absorption spectroscopy using the carbon rod was the method used for sample analysis. Results indicated that, based on finding lead in the nitric acid scrubbers, lead collection efficiencies on the filter decreased at greater distances from the street. Intrigued by studies of Spurny et al., who showed that membrane filters tend to pass some of the aerosols in the 0.1- to 0.4-μm range, Dr. Skogerboe made some lead measurements and systematically varied the face velocity. The results indicated drop-off in collection efficiency with increasing face velocity.

Then the speaker described the use of a condensation nuclei counter to check filter efficiencies. No particles were detected coming through the filters. New sampling trains were set up consisting of a millipore filter (0.45-μm pore size) backed by a graphite filter and a nitric acid scrubber and using the same rate and time as mentioned previously. From 2 to 30 percent of the total lead was found in the charcoal traps, and greater percentages were found in the scrubbers (6 to 53 percent), depending on the distance from the street. Dr. Skogerboe concluded from these results that the lead reaching the scrubbers must be organic (gaseous), which is either not trapped by activated charcoal or, if it is trapped, gets "eluted" from the charcoal by the air stream. He also presented data indicating that iron and cadmium get through the filters.

Dr. Skogerboe also discussed work that was done prior to the field sampling experiments to determine the extent of the lead blank in

the millipore and graphite filters and in the nitric acid. These values were as follows:

Millipore filter	0.082 ± 0.010 µg Pb/filter
Graphite filter	<0.001 µg Pb/filter
Acid scrubber $[HNO_3/H_2O$ (1:1 v/v)]	0.00042 µg Pb/ml

Comparing these levels to the data collected in the field experiments showed that concentrations well in excess of the blank levels were collected.

Dr. Skogerboe presented four graphs depicting the correlations between membrane filter efficiencies and filter loading for Pb, Fe, and Cd collected at a constant flow rate. The results showed that as the filter load increased, the collection efficiency increased, possibly due to the decrease in pore size of the filter because of loading.

Dr. Skogerboe concluded with the statement that he plans to conduct further studies intended to give more definitive explanations for what he has observed.

Reed Robertson and James Hickey -- Nalco Chemical Company

The sampling train described by Mr. Robertson consisted of a glass fiber or membrane filter, an activated carbon scrubber, and two impingers in series containing either nitric acid in both or nitric acid in the first and iodine monochloride in the second. This system was used to collect a minimum of 15 to 20 cubic meters of air in 24 hours. High-purity nitrogen and pre-filtered laboratory air were used to determine average blank values. Lead was added to the activated carbon in both laboratory and field tests, and recovery studies were performed. A known amount of organic lead vapor was generated, and this was collected by the sampling train. Following analysis of the samples, recovery percentages were calculated. Efficiencies of the nitric acid scrubber and iodine monochloride scrubber for organic lead were evaluated by using the sampling train with the activated carbon scrubber removed.

Based on the results of the studies outlined, the speakers drew the following conclusions. Lead found in blanks (equivalent to 0.06 ug/m^3) is insignificant with large samples (20 m^3) of air. Glass fiber filters pass less than 2 percent of the total lead catch, and millipore filters pass less than 1 percent. No lead was found on the activated carbon trap or in the nitric acid or iodine monochloride impingers; but if any were found, it would be less than the amount in the blanks. The ASTM procedure for treating activated charcoal recovers lead added to carbon, 98 to 102 percent by material balance. An iodine monochloride scrubber is much more efficient for collecting lead than is a nitric acid scrubber. The use of glass fiber filters in conjunction with high volumes of sample represents the most efficient sampling technique available at the present state-of-the-art, according to Mr. Robertson.

Gary Ter Haar and Manuel Brandt -- Ethyl Corporation

Mr. Ter Haar described a filtration system for atmospheric lead which consisted of a glass fiber or membrane filter followed by activated carbon and a pair of scrubbers, one containing 3N nitric acid and the other empty. Samples were taken in parallel at 0.75 and 15 liters/minute for 24 hours at three locations. In another filtration study (flow rate 0.75 liter/minute) membrane and glass fiber filters were followed by activated carbon and a liquid nitrogen trap. In another study the efficiency of Mine Safety Appliance (MSA) activated carbon (Stock No. 24207) for tetraethyl lead (TEL) or tetramethyl lead (TML) was tested.

Lead in each sample was determined by atomic absorption after complexation with sodium diethyldithiocarbamate and extraction into methyl isobutylketone. At least one blank of each sample type was run with each group of analyses. Average blank values were used to correct gross results.

The speaker concluded from the data collected in the studies that both types of filters demonstrate high efficiency for the collection of particulate lead and that only a low percentage of organic lead exists, especially where lead concentrations are somewhat elevated or when the higher sampling rate is used. At the lower sampling rate, it was found that the backgrounds on carbon and acid were too large a part of the total lead found to give dependable results. The blank values were reported as follows:

Glass fiber or membrane filter	0.9 µg Pb/filter
Carbon	2.0 µg Pb/2 g sample size
Acid scrubber (3N HNO_3)	0.2 µg Pb/ml

These blank values include the filter and carbon or acid plus the chemicals needed to bring these samples to the point of analysis. When a sample of 3N nitric acid was analyzed directly by a flameless atomic absorption technique, the total acid blank was 0.001 to 0.008 µg Pb/ml. However,

even at the lower sampling rate where blanks values became significant, average filter efficiencies were high, and organic lead was low. Although Mr. Ter Haar mentioned that the blanks were higher than he would have liked, he stressed the importance of sufficient sample size to make the blanks a small part of the total sample.

In the cryogenic study, Mr. Ter Haar reported that lead which passed through the filter averaged only 2 percent of the total lead collected. It was also mentioned that activated carbon quantitatively retained both tetramethyl and tetraethylead, as shown by the MSA study.

The speaker closed with the statement that both glass fiber and membrane filters are highly efficient in collecting particulate lead in air and that the small amount of organic lead present is efficiently collected on activated carbon. The studies of Drs. Robinson and Skogerboe indicate that measurements of lead as reported by the National Air Sampling Network are low because of lead passing through the filter; according to Mr. Ter Haar, this is not so.

Ralph Parod — Environmental Health Laboratories, Inc.

Mr. Parod discussed filter efficiency for lead particulate. The sampling train used to collect freeway samples consisted of a 0.45-μm millipore filter followed by two nitric acid scrubbers in series. The flow rate varied from 4.6 to 10.4 liters/minute. Mr. Parod also reported results obtained using a closed system for the generation and collection of lead particulate. The particulate was generated by burning an alcoholic solution of organic lead (TEL). The collection system consisted of a glass fiber or millipore filter (0.45 μm), an activated charcoal trap, and two nitric acid scrubbers in series. The flow rate varied from 7 to 9 liters/minute.

The concentration of lead in each sample was determined by the colorimetric dithizone procedure.

The data acquired from sampling near a freeway showed filter efficiency for particulate lead to be on the order of 97 percent, whereas the studies on the closed system, in which lead particulate was generated and collected, showed efficiencies for glass fiber and millipore filters approaching 99 percent. Blank values reported were as follows:

Millipore filter	0.025 μg Pb/filter
Glass fiber filter	0.5 μg Pb/filter
Activated charcoal	0.5 μg Pb/g
Acid scrubber (10% HNO_3)	0.0006 μg Pb/ml

E. S. Jacobs -- DuPont Company

Dr. Jacobs described the sampling train used for collection of atmospheric lead as consisting of a millipore filter followed by either an activated charcoal scrubber or one containing iodine monochloride. Lead was extracted from the filter and scrubbers and analyzed by atomic absorption spectroscopy. Results of field studies at five sampling sites were presented. Also described were studies to determine the amount of non-filterable lead in vehicle exhaust in 1963 to 1970 automobiles and experiments designed to determine the mass balance of lead burned in various engines.

The speaker concluded from his data that only 1 to 3 percent of total lead in the air and less than 0.1 percent of exhaust lead may pass through a filter. The particulate lead concentration in car exhaust was shown to be 100 to 1,000 times greater than that of the organic lead. The lead balance study on cars which ran for 50,000 or more miles accounted for better that 95 percent of all the lead used during this mileage accumulation.

Clair C. Patterson -- California Institute of Technology

Dr. Patterson did not deliver a prepared talk, but instead commented on the material that had been presented. He observed that the researchers with low blanks found lead that passed through the filter, while those with high blanks did not. He emphasized the importance of low blank values for measurement methods of the type discussed.

As an explanation for the high freeway levels of lead found by some researchers, the speaker also commented on the possibility of large amounts of lead-containing particulate depositing on the road and being volatized under appropriate meteorological conditions.

Dr. Patterson also discussed a cooperative experiment with Dr. Robinson whereby he would visit the Baton Rouge Laboratory and collect samples for analysis as Dr. Robinson is monitoring. Dr. Patterson would return to his laboratory and assay those samples that were collected at the same time that Dr. Robinson was monitoring a high "molecular lead" value by an isotope dilution mass spectrometric technique. This experiment would ascertain the accuracy of Dr. Robinson's total lead measurement.

Benjamin Y. H. Liu -- University of Minnesota

Dr. Liu discussed the subjects of size distribution of particles and filter efficiencies. He presented a slide containing a plot of particle volume versus particle diameter for fresh auto exhaust that showed a peak between 0.01 and 0.1 μm. He mentioned that the percentage of particle volume associated with submicron particles varies from 9 percent in Fort Collins, Colorado, to 69 percent in Los Angeles, California.

On filter efficiency, Dr. Liu reported that when using a 10-μm pore size Mitex Teflon filter, the minimum efficiency for collection of 0.05-μm particles was found to be 65 percent at 1 cm mercury pressure drop. For a 5-μm pore size of the same filter and using the same particle diameter, the minimum collection efficiency was reported to be 80 percent at 1 cm mercury pressure drop. For both pore sizes of filters, as the pressure drop was increased, the particle size for minimum collection efficiency shifted to smaller sizes. In addition, when using 8-μm pore size Nucleopore filters, the efficiency for collection of 0.02 to 0.1-μm particles was found to be 0 percent at 1 cm mercury pressure drop, increasing to 20 percent at 25 cm mercury pressure drop. Further, Dr. Liu reported that preliminary measurements on 0.8-μm millipore filters show that the collection efficiency is essentially 100 percent. He also mentioned that he would like to get some of Dr. Robinson's Micropore carbon discs and examine them for collection efficiency.

DISCUSSION

As mentioned previously, this seminar had a double purpose:

1. To review current methods for sampling and analyzing atmospheric lead.
2. To consider the latest research data by Drs. Robinson and Skogerboe suggesting that large quantities of lead pass through the filters being used to measure lead in air.

This lead is termed "organic (gaseous)" by Dr. Skogerboe and "molecular" by Dr. Robinson.

With regard to the second objective, Dr. Jacobs and Messrs. Parod, Ter Haar, and Robertson presented data indicating that greater than 95 percent of the total lead is collected on the primary filter and that the small percentage of organic lead that exists is efficiently collected on the secondary carbon filter.

In attempting to compare the results presented, one finds a number of problem areas. The type of filter for collecting samples varied (millipore, glass fiber, membrane) as did the blank value of the different filters. Various types of carbon backup filters were used. The nitric acid in the scrubbers ranged from doubly redistilled to reagent grade, and the concentration also varied from investigator to investigator. Flow rates and sampling times varied from 100 ml/minute for 5 minutes to 15 liters/minute for 24 hours. Further, samples were analyzed colorimetrically as well as by four different techniques of atomic absorption spectroscopy. According to Dr. Robinson, humidity had an effect on the amount of "molecular" lead observed, but no other investigator recorded its value. Dr. Liu indicated that the concentration of submicron-size particles can vary from 9 to 69 percent depending on the part of the country in which samples are collected. The statements by Drs. Robinson and Liu suggest locational effects on results.

Therefore, any attempt to compare these results for atmospheric lead is most difficult, because the researchers used different filter

media, sampling rates, sampling times, reagent purities, and analytical methods. In addition, sampling locations were different.

CONCLUSIONS

The conclusions that can be drawn from this seminar are very clear. There is wide variability in the sampling and analytical parameters for the analysis of atmospheric lead. More work must be done to determine the effects related to filter media, sampling velocity, sample handling, and humidity. In addition, substantiation by an independent investigator and unequivocal characterization of the structure(s) of "molecular lead" (Robinson) and the nature of the "gaseous lead" (Skogerboe) are vitally needed. Only through more research and vital confirmation studies will we be able to determine the true atmospheric profile of lead.

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